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Micropatterning of nanoparticle films by bilayer lift-off

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Abstract

Nanostructured films are deposited by a new technique that matches supersonic cluster beam deposition with flame spray pyrolysis production of nanoparticles (FlameBeam). These films are structured with micrometric lateral resolution, applying a lift-off method by pre-structuring a photoresist-PMMA bilayer with a suitable 'mushroom-like' cross-section, depositing a nanostructured silver film on top and lifting off the bilayer in an aqueous solution. Optical inspection revealed that line-shaped microstructures, having a minimal width of up to 3 μm, can be successfully obtained. The nanostructured films have survived the aqueous treatment, as demonstrated by electron microscopy imaging and electrical characterization through 4-point measurement method (Van-der-Pauw). The latter has been possible through sputtered gold pads that were realized on the substrate prior *to* the deposition of the photoresist and of the nanostructured film. These results disclose novel possibilities in the fine patterning of FlameBeam-deposited films and their integration into microelectromechanical systems devices in general.

Keywords: FlameBeam, nanoparticle films, lift-off, PMMA, photoresist

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanostructured films have progressively gained in importance due to their extraordinary property of high surface-area-to-volume ratio and to the recent availability of new deposition techniques that allow deposition in a reliable and controllable way. Among aerosol-based techniques for the deposition of nanostructured films, cluster beam deposition became particularly attractive because of its peculiarity to perform direct deposition of nanoparticles at room temperature, onto any kind of substrate, with intensities well beyond the needs of basic research and compatible with various industrial applications [1–3]. In order to exploit the peculiar properties of this nanomaterial, in the recent years much effort has been spent integrating them into micro-devices [4] and nanodevices [5]. To fulfil this goal, a good control of the patterning of nanoparticle deposition, with respect to pre-existing structured layers, should be provided.

Conventionally, micro-devices are patterned by applying a photoresist, structuring it and transferring this structure onto a pre- or post-deposited thin film by wet/dry etching or lift-off. However, these processes include several heating and wet-chemical treatments, which may affect the granularity and porosity of the nanostructured films [6, 7]. For this reason, alternative patterning methods have been exploited: in the 100 nm range and below, structures were achieved by attracting the nanoparticles onto pre-charged surface areas [8, 9], and by electrostatic focusing of charged nanoparticles [5]; in the micrometre range the structuring was achieved by placing shadow masks in front of the nanoparticle beam [2, 10].

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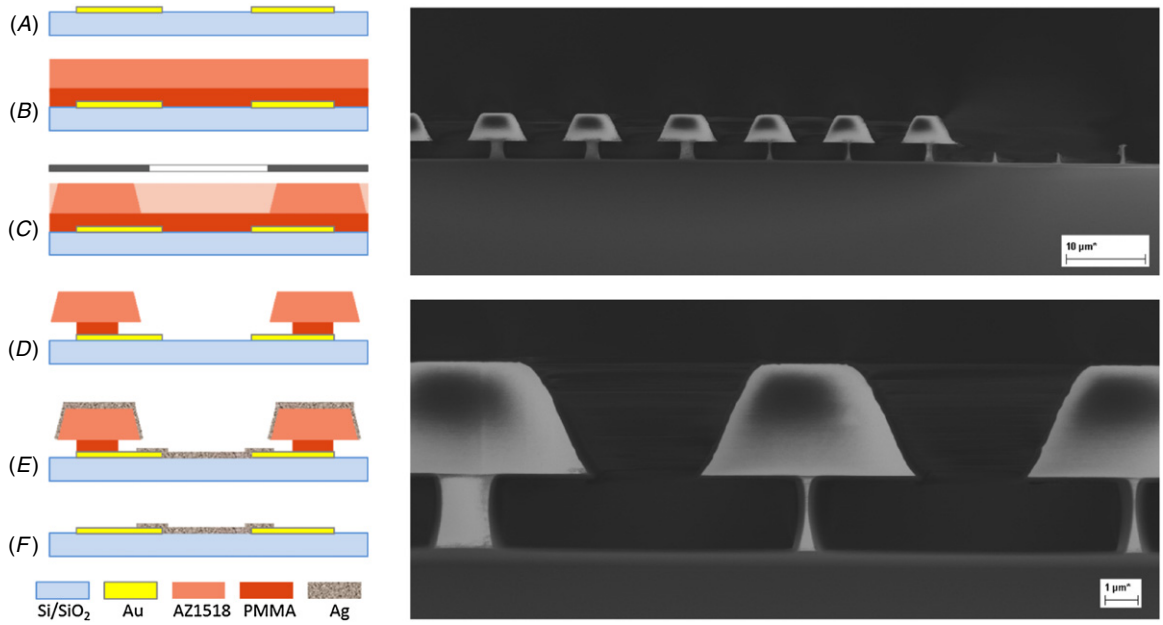

Figure 1. Left: flow diagram of the bilayer lift-off method: (*A*) spin of the bilayer, (*B*) UV illumination, (*C*) bilayer structuring, (*D*) FlameBeam silver cluster deposition, (*E*) bilayer lift-off. Right: SEM images of the bilayer lift-off method, taken directly after step C in the flow diagram.

However, in the micrometre range a high-precision alignment of hard mask with respect to pre-existing structures on the substrate is a challenge with decreasing structure size.

Recently, bilayer lift-off techniques have been introduced for the fabrication of e.g. quartz-based capacitive sensors [11] and structuring of carbon-nanotube films [12]. Researchers used a two-layer stack, whereas the bottom layer is undercut during photoresist development, to provide a better stack lifting.

This paper presents the successful application of the above mentioned bilayer lift-off technique in the micro-structuring of silver nanoparticle films, deposited by FlameBeam [13], a gas-phase deposition method based on a suitable coupling between a flame spray pyrolysis (FSP) source and a vacuum-driven nozzle expansion, that generates a supersonic nanoparticle beam. The first part of the paper describes the structuring of the bilayer, followed by a description of the FlameBeam silver deposition technique. Morphological and electrical characterization of the obtained microstructures by electron microscopy and Van-der-Pauw [14] resistivity measurements are reported.

2. Fabrication process

2.1. Bilayer lift-off method

The micropatterning of nanoparticle-assembled films is performed by a bilayer lift-off method: a stack of PMMA and photoresist is spin-coated and structured into moulds with a 'mushroom-like' cross-section. On top, a nanoparticle-assembled film is deposited by FlameBeam and the bilayer is removed in an aqueous solution, thus shaping the nanoparticle-assembled film into lines and clover leaves. The lines are used for resolution inspection, and the clover leaves are needed for electrical test. In order to ensure reliable electrical contacts, prior to bilayer spin-coating, gold pads are realized under the edges of the to-be-realized clover leaves.

The flow diagram of the bilayer lift-off method is presented in the left image in figure 1. As a substrate a 4 inch, 525 μm-thick Si wafer with a 500 nm-thick SiO_2 is used. An 80 nm-thick gold film is sputtered and structured into contact pads by a 1.8 μm-thick AZ1518 photoresist mask and wet etched in iodine solution (0.1 mol L^{-1}), as depicted in figure 1(*A*). Then, a 2.1 μm-thick PMMA film (ARP 5460) is spin-coated on the substrate (12 s@500 rmp and 60 s@1000 rpm) and heated in an oven for 30 min@150 °C. This thermal treatment removes the solvents from the PMMA layer. Next, a 3.9 μm-thick positive AZ1518 photoresist is spin-coated (12 s@500 rpm and 45 s@1000 rmp). The stack is heated in an oven for 30 min at 90 °C (figure 1(*B*)) and UV-illuminated through a quartz–chromium mask (figure 1(*C*)). The UV-light interacts only with the photoresist through the mask transparent areas. This interaction increases the solubility of the photoresist in developer solutions and does not alter the properties of the PMMA bottom layer. Next, the stack is treated with a photoresist developer (AZ 726 MIF), which removes the illuminated portions of the photoresist layer. When the developer reaches the PMMA layer, the developer starts to etch it isotropically. The result is an 'undercut structure' with a 'mushroom-like' cross-section, as shown in figure 1(*D*). A nanostructured silver layer is then deposited by FlameBeam technology by simply exposing the pre-structured sample directly to the nanoparticle beam, in vacuum conditions, at room temperature (figure 1(*E*)). After the deposition session, the PMMA-photoresist stack is completely removed by a DFA remover (Walter Lemmen GmbH), applied for 15–30 min@50 °C. This generates nanostructured silver lines and clover leaves onto the substrate surface (figure 1(*F*)).

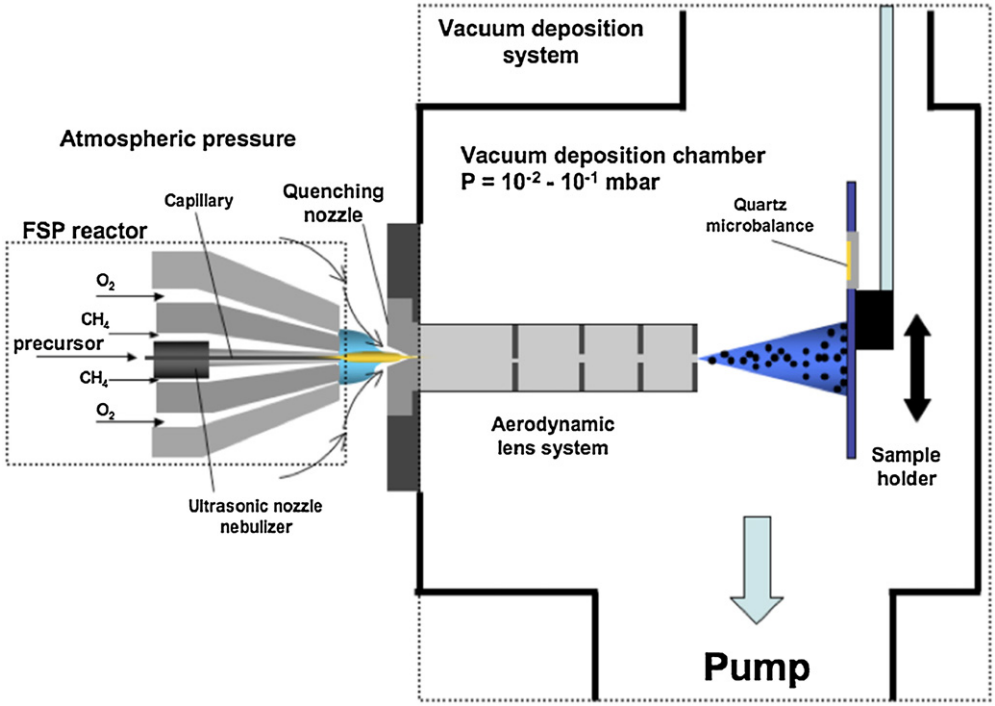

Figure 2. Schematic representation of FlameBeam cluster deposition system. Reprinted from [13] with permission.

The micropatterning of the bilayer strongly depends on the duration of the developing process. In order to achieve lines with minimal width, the bilayer was structured by rotating the wafer at constant speed and letting the developer solution be sprayed on it. The development time is a critical parameter, whereas in a narrow time slot of 35–38 s the 4 –6 μm lines can be completely undercut and swept away during the rinsing process. In order to slower the reaction, we diluted the AZ 726 MIF solution MIF (1:4) and manually developed it in a petri dish. This led to a much slower development and thus undercut rate, however brought a highly inhomogeneous development rate overall the whole wafer.

The structuring of the bilayer was inspected by scanning electron microscopy (SEM) (right images in figure 1). The top right image represents the cross-sections of several PMMA-photoresist lines directly after the developing process step. Starting from the left, the first three lines had an original width of 4 μm, the middle three lines were 5 μm wide and the last three lines were 6 μm. The PMMA-layer of the narrowest lines of 4 μm original width was completely etched away by the developer. The bottom right image shows a magnification of the lines, whereas a portion of the 5 μm-wide lines and a 6 μm-wide line can be seen.

2.2. Deposition of nanostructured silver layers

Nanostructured silver layer was deposited by FlameBeam. This is a new technique that consists of nanoparticle generation by FSP and their subsequently in-vacuum deposition throughout a supersonic cluster beam apparatus. In the following an overview of the technology is reported; additional details can be found in [13].

The FlameBeam apparatus consists of a FSP reactor [15, 16] for the generation of nanoparticles, coupled with a supersonic cluster beam deposition system [1]. The coupling is obtained through a critical flow expansion nozzle, named quenching nozzle, which separates the ambient-pressure/high-temperature particle synthesis flame from the low-pressure/room-temperature deposition chamber, as schematically shown in figure 2.

At the conical inlet of the quenching nozzle, the nanoparticle-laden flame first contracts and then expands in vacuum through the nozzle. As a peculiar characteristic of the FlameBeam method, a sheath made of ambient air, surrounding the nanoparticle-laden flame, effectively prevents the sticking of the nanoparticles onto nozzle surfaces and avoids nozzle clogging.

A pressure difference larger than 500 mbar leads to critical flow conditions and quenching of the flame aerosol by expansion and mixing with the air, which rapidly stops nanoparticle growth. Subsequently, the quenched aerosol passes through a second nozzle consisting of an aerodynamic lens system [17] that accelerates and, most importantly, focuses the nanoparticles to a collimated beam of ~25 mm diameter at the substrate [13]. This shifts the deposition regime from diffusion towards directed impaction at nearly room temperature.

The liquid precursor solution is delivered to the FSP reactor by a syringe pump at a rate of 0.12 mL min^{-1} (2 μL s^{-1}). The liquid precursor was prepared by mixing silver nitrate, $AgNO_3$, into ethanol at 0.04 Ag^+ molar concentration. The FSP reactor consists of an ultrasonic nozzle nebulizer that atomizes the liquid precursor without relying on a dispersion gas, in contrast to conventional FSP. The droplets produced by ultrasonic atomization were entrained by a concentric diffusion

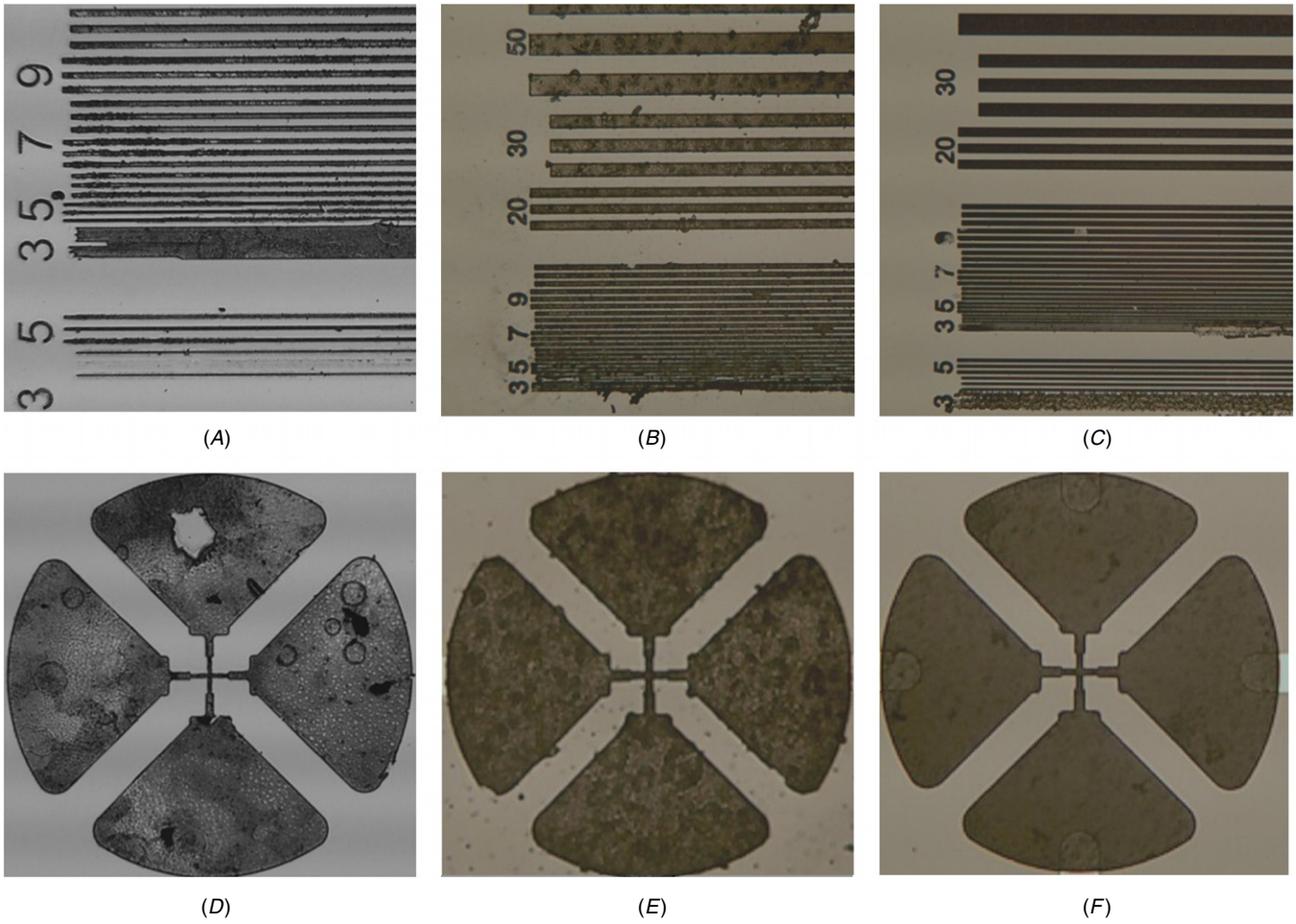

Figure 3. Silver films structured into lines with widths varying from 3–10 μm (upper row) and clover-leaves with minimal widths of 5 μm (bottom row).The thickness of the deposited films is: (*A*) 1 μm, (*B*) 500 nm, (*C*) 100 nm, (*D*) 1 μm, (*E*) 500 nm, (*F*) 100 nm.

flame formed from co-flowing 0.12 L min^{-1} of methane and 0.5 L min^{-1} of oxygen that were delivered from cylinders by calibrated mass flow controllers. In the diffusion flame, droplet species evaporated and combusted leading to formation and growth of silver nanoparticles.

The silver nanoparticles were thus collected on the substrate to form the nanostructured film, by exposing the substrate (that was previously prepared as 'undercut structures' formed during developer action on bi-layered photoresist) to the nanoparticle beam. In order to control the thickness of the nanostructured film during the deposition, the sample holder is equipped with a quartz microbalance. A suitable beam-rastering process ensures that the microbalance is exposed to nanoparticle beam exactly as the substrates do. In this way the thickness of the nanostructured film can be real-time monitored and the deposition process can be stopped once the target thickness is reached. The low kinetic energy at the nanoparticle-substrate impact preserves the original structure of the nanoparticles and causes their soft-assembling leading to the formation of a nanostructured film. During the deposition, the substrate temperature is expected to slightly increase above room temperature due to the exposition to the nanoparticle beam. However this is not expected to cause any damage to the PMMA/photoresist bilayer.

In this study, the FlameBeam method was applied for the deposition of nanostructured silver films having thicknesses of 100 nm, 500 nm and 1 μm.

3. Lift-off characterization

After the deposition of nanostructured silver films, the samples were inserted into a liquid remover (15–30 min@50 °C, DFA remover) and the PMMA-photoresist bilayer was removed, structuring the silver film into lines of 3–50 μm-width (top row in figure 3) and clover leaves with 5, 10, 50 and 100 μm-wide crosses (clover leaves with 5 μm-wide crosses are shown in bottom row in figure 3). In figure 3, the film thickness is 1 μm in A and D, 500 nm in B and E and 100 nm in C and F.

In the case of the clover leaves, structured from 1 μm-thick silver samples, we observed poor film adhesion, as highlighted by figure 3(*D*), where a roundish portion of the film detached from the upper leaf. To improve film-substrate adhesion, we introduced an oxygen plasma treatment (500 sccm O_2 flow, 500 W, 30 s, 400 PlasmaSystem, Technics Plasma GmbH) of the substrates, prior to silver deposition, aiming to remove

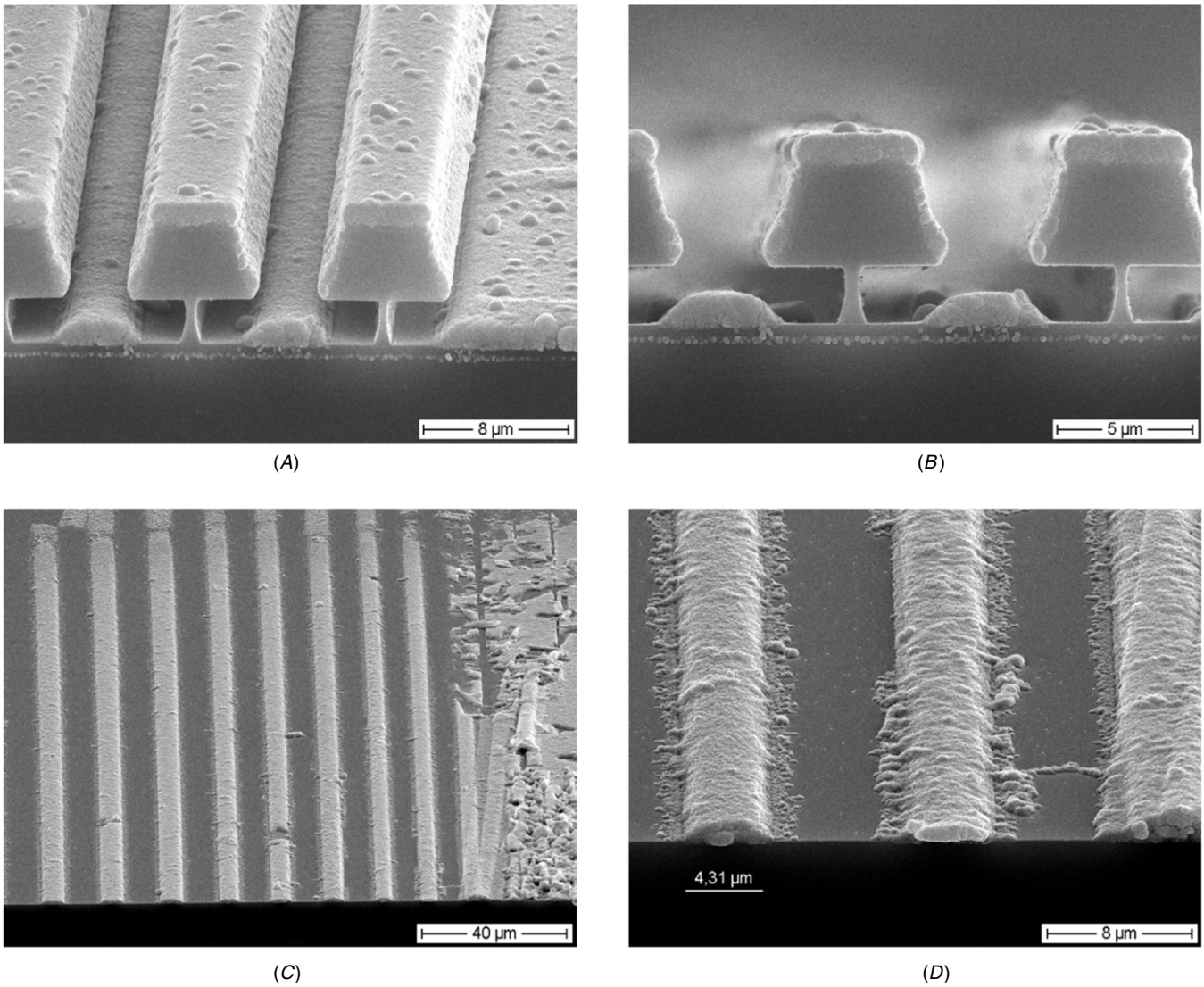

Figure 4. (*A*) and (*B*): SEM images before lift-off of 1 μm thick silver films, deposited onto photoresist mushroom-structures. *(C)* and *(D)*: SEM images after lift-off of 1 μm thick silver films, structured into lines. Minimal line width is 4 μm (without fringes) and 5 μm (with fringes).

any PMMA residue, which may still be present on substrate surface after the development process. As a side effect of the oxygen plasma, we observed a slight widening of the PMMA-photoresist undercuts and thus a slight increase of the gaps between the lines.

Figure 4 shows SEM images of the 1 μm-thick sample after deposition of nanostructured silver (top row), and after lift-off (bottom row). The obtained minimal line width after lift-off is 4 μm (without fringes) and 5 μm (with fringes), as it can be seen in figure 4 in the lower right image.

In order to verify whether the nanoscale morphological features of the nanoparticle-assembled films are preserved after the lift-off process, we performed SEM imaging of sample surface, as shown in figure 5. Nanoscale surface roughness and porosity, as well as a surface morphology characterized by a nanosized grain structure, as commonly observed in as-deposited samples by FlameBeam [13] and other supersonic cluster beam deposition methods [18], demonstrate that the peculiar features of this kind of nanostructured films survive the lift-off process.

4. Electrical characterization

The nanostructured silver layers were electrically characterized according to the Van-der-Pauw method, which offers an accurate measurement of the specific resistivity of thin film structures of arbitrary shapes, provided the contacts are small and are situated at the edges of the structure, and the structures are of symmetrical form, of uniform thickness and of homogeneous composition [14].

The usual approach of Van-der-Pauw method in the case of compact films (such as those obtained by sputtering process), where the specific resistivity of a film is measured by directly contacting it with micro-manipulated needles, cannot be adopted in the case of nanoporous soft-assembled films, as those of the present research, for the unreliability of the contacts. Therefore, in order to ensure good and reliable

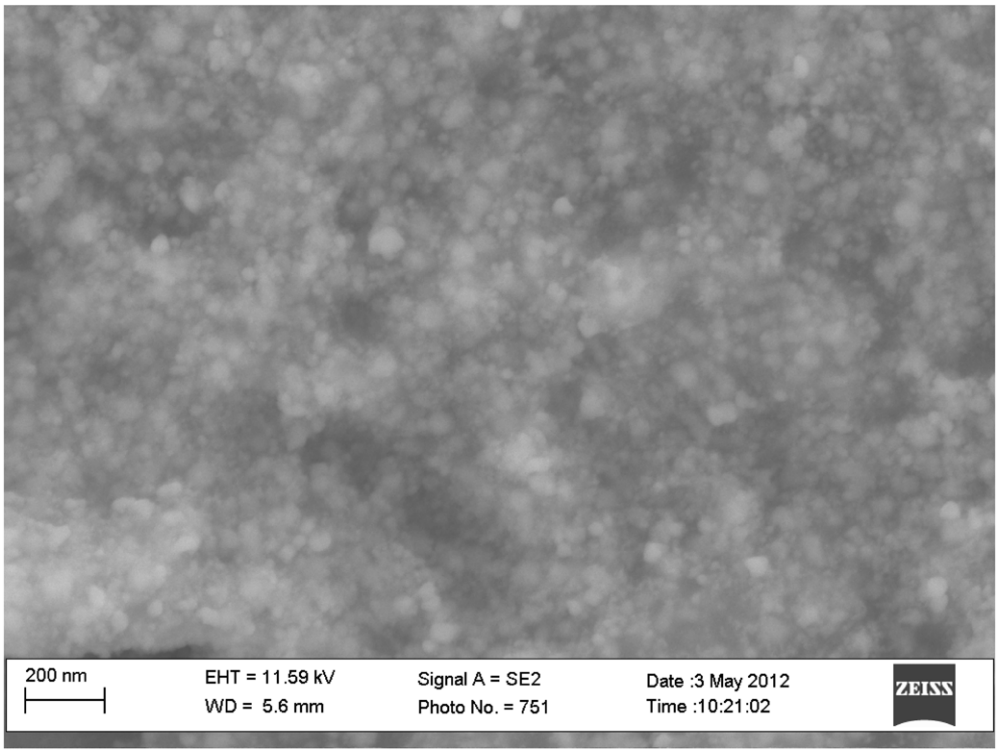

Figure 5. SEM image of the nanostructured silver film surface at sub-micrometric scales after lift-off.

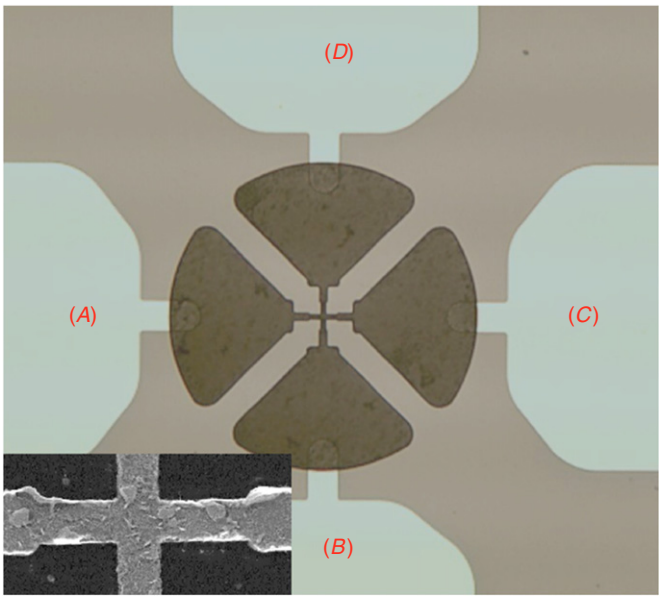

Figure 6. Cover leaf structure for electrical measurements. Elements A, B, C, and D are pre-deposited gold pads to ensure reliable electrical contacts with the nanostructured film. The inset shows a SEM image of the central structure.

electrical contacts on the nanostructured silver films, we first deposited a thin film of gold and structured it into pads. The obtained silver clover leaf together with the gold contact pads are shown in figure 6.

In order to obtain the specific resistivity according to Van-der-Pauw, a current is fed through the points A–B of the structure in figure 6, and the voltage drop is measured across C–D. By measuring two resistances ($R_{AB,CD}$ and $R_{BC,DA}$) the specific resistivity of the sample is determined as follows

$$\rho = \frac{\pi d}{\ln 2} \frac{\left(R_{AB,CD} + R_{BC,DA}\right)}{2} f\left(\frac{R_{AB,CD}}{R_{BC,DA}}\right)$$

whereas d is the thickness of the thin film and f is a correction factor between 0 and 1 [9]. A Keithley 199 System DMM Scanner was used to carry out these measurements.

Four different clover leaf shapes, made of nanostructured silver having the same thickness of 500 nm and minimal line width of 5, 10, 50 and 100 μm, were subjected to resistivity measurements. Samples having minimal line width of 50 and 100 μm show resistivity values of about 1×10^4 nΩm, while samples with minimal line width of 5 and 10 μm show much larger resistivity values exceeding 1×10^{10} nΩm.

5. Discussion

Successful results in microstructuring the silver films through lift-off process, as demonstrated in figure 3, confirm that the PMMA/photoresist bilayer, created with the standard process described in section 2 of this paper, is fully compatible with the FlameBeam deposition method: no damage occurred to the bilayers during the exposure to the flame-generated nanoparticle beam. As it happens in general in thin film deposition by supersonic cluster beam, no matter the kind of nanoparticle source is used, the energy delivered at the impact of the nanoparticles with the substrate is negligible also in the case of FlameBeam.

No serious adhesion problem was observed after lift-off for samples having thickness as large as 1 μm. This may be ascribable to the fact that the grain nanostructure

of the films, resulting from soft-assembling of nanoparticles, favours the relaxing of the mechanical stresses generated during film growth, which is the main mechanism leading to the detachment of compact films from their substrates.

The limitations of the lift-off process with respect to minimum achievable width of silver lines can be divided in two cases. In the first case, when the line width is equal to the distance between neighbouring lines, the maximum line resolution is 5 μm, being limited by the thickness of the PMMA. During the developing process, the PMMA layer is etched isotropically e.g. in case of a 2 μm-thick PMMA layer, the minimal achievable PMMA-resist line is of 5 μm width (the PMMA layer is undercut at both sides by 2 μm, resulting in a 1 μm-wide PMMA 'trunk'). Narrower structures are mechanically not stable enough; they will either collapse or will be flushed away during the developing process. Furthermore, the silver line width could be further reduced to 2 μm for thinner silver layers e.g. layers of 100–200 nm thickness could be structured by a 0.4 μm-thick PMMA film. In the second case, when the line width is smaller than the distance between neighbouring lines, a minimum silver line width of 3 μm is achieved (with a 10 μm distance between the lines). These results disclose the possibility to adopt FlameBeam for the direct integration of nanostructured–nanoporous functional layers in micromachined devices, such as for example chemoresistive metal-oxide gas sensors. In fact, batch deposition of miniaturized devices typically requires that functional material is patterned in specific regions of the device platforms, over a large number of platforms at the same time.

As already shown in figure 5, post lift-off investigations of film surfaces at sub-micrometre scales reveal peculiar morphological features, ascribable to ballistic growth [16] as expected in low-energy supersonic cluster beam deposition. In particular, a surface roughness characterized by a nanosized grain structure and porosity, demonstrate that the lift-off process is safe for the survival of the peculiar morphological properties of this kind of nanostructured films.

Although resistivity values are several orders of magnitude larger than the value of bulk silver (1.6×10^{-8} Ωm = 16 nΩm), electrical measurements demonstrate the substantial absence of discontinuities (such as for example cracks) in the microstructures after lift-off process. High values of resistivity may be ascribable to the nanostructure generated by nanoparticle soft-assembling growth mechanism of this kind of films, where electrical conduction takes place only through percolative paths connecting nanoparticles at their grain boundaries point of contact [19].

The resistivity of the 5–10 μm wide lines is several orders higher than the one of the 50–100 μm wide lines. This may be due to phenomena related to the lift-off process itself. We assume that the aqueous solution, needed to remove the PMMA-photoresist stack during lift-off, may have penetrated up to a certain depth into the silver film and thus modified its nanostructure by further separating the nanoparticles from each other. This modification occurs most probably on the silver's surface rather than within the whole volume, which would explain the several-orders-higher resistivity of the small-line-width structures, compared to the wider ones. A deeper comprehension of the behaviour of the electrical conduction with respect to the dimensions of the microstructured elements needs further investigation.

The proposed lift-off method can be successfully applied for the structuring of thin films up to a certain safety margin, defined as the delta thickness of PMMA minus the silver film. We conducted experiments with silver films of maximum 1 μm thickness. In this case a 2 μm-thick PMMA layer i.e. a 1 μm safety margin was more than enough. In order to lift-off thicker silver layers, one could increase the PMMA thickness up to 3 μm, then deposit silver layers of up to 2–2.5 μm thickness and thus work with a safety margin of up to 0.5 μm. However, thicker PMMA layers will result in a slightly broader line width and they will require a larger line pitch. Furthermore, a decrease in safety margin would raise the probability of lift-off defects.

6. Conclusions

In this paper we demonstrated that the FlameBeam deposition technique for the production of nanostructured–nanoporous films is fully compatible with micropatterning by a PMMA-photoresist lift-off technique. Both room temperature deposition condition and negligible substrate heating due to nanoparticle beam allow the deposition to take place over polymeric materials such as photoresists and PMMA. Adhesion is strong enough to prevent any film damage during lift-off process, up to film thicknesses of 500 nm. We demonstrated that nanostructured coatings by FlameBeam can be successfully patterned with micrometric lateral resolution. Electrical conduction measurements confirm the integrity of the microstructures, as well as the nanostructured nature of the films related to the soft-assembling of nanoparticles during film growth.

Provided the extremely wide library of materials that can be processed by FlameBeam in form of nanostructured–nanoporous layers (ranging from simple oxides to spinels to complex oxides, from pure noble metals to oxide-supported noble metananostructurels), this research may disclose novel opportunities in the field of nano-on-micro, i.e. the integration of nano-enhanced functional layers in miniaturized devices, with potential applications including chemical sensing, biosensing, mechanical transducing, gas gettering, etc.

Acknowledgments

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